Anomalous pH Dependent Stability Behavior of Surfactant-Free Nonpolar Oil Drops in Aqueous Electrolyte Solutions

Lucy Y. Clasohm,[†,‡] Ivan U. Vakarelski,[†] Raymond R. Dagastine,*,[‡] Derek Y. C. Chan,[§] Geoffrey W. Stevens,[‡] and Franz Grieser*,[†]

Particulate Fluids Processing Centre, School of Chemistry, Department of Chemical and Biomolecular Engineering, and Department of Mathematics and Statistics, University of Melbourne, Parkville, Victoria 3010, Australia

Recent advances in atomic force microscopy (AFM) force measurement techniques have allowed the direct measurement and theoretical interpretation of the interaction between a liquid droplet and a solid surface or between two liquid droplets. In this study, we investigated the interaction across an aqueous thin film between fluorocarbon (perfluoropentane) droplets, hydrocarbon (tetradecane) droplets, and a droplet and a flat mica surface in the absence of stabilizers. It was found that even at a relatively elevated electrolyte concentration of 0.1 M NaNO$_3$, depending on the solution pH, interactions between two identical droplets or a droplet and a mica surface could be repulsive. A simple theoretical analysis of the magnitude and range of these interactive forces suggests that the DLVO theory cannot explain the observed behavior. The measured force behavior is discussed in the context of ion adsorption, and the arising charging effects, at the bare oil–water interface.

Introduction

An understanding of the interaction forces between emulsion droplets in aqueous solutions at elevated electrolyte concentrations is of significant fundamental and practical interest.[1] Such solution conditions are characteristic of physiological systems and a number of industrial applications, including food processing, pharmaceuticals, and cosmetics manufacturing. In typical commercial products, emulsion droplets are stabilized by surface active additives; however, it is also known that nonpolar oil droplets in aqueous solutions can acquire a significant negative charge even in the absence of surfactant stabilizers.[2–4] Here, we employ atomic force microscopy (AFM) to study the interaction between two nonpolar oil droplets and between an oil droplet and a solid substrate, in the absence of surfactant additives in aqueous solutions at elevated electrolyte concentrations. We have investigated two types of oils: a hydrocarbon oil (tetradecane, C$_{14}$H$_{30}$), a liquid with a higher refractive index than water, and a fluorocarbon oil (perfluoropentane, C$_5$F$_{12}$), a liquid with a lower refractive index than water. The difference in the optical properties of the oils meant that we were able to manipulate the short-range van der Waals interaction between the drop and a flat mica surface across an aqueous electrolyte solution. From theoretical considerations, one can expect that the interaction will be attractive for the hydrocarbon oil and repulsive for the fluorocarbon oil.

Traditional methods for investigating the interaction between emulsion droplets across thin liquid films include simple measurements of the coalescent time between a droplet and an oil phase[5] and a number of interferometric thin liquid film cell

techniques.[6–8] Newer experimental methods include a modified surface forces apparatus[9] and the alignment of droplets in magnetic fields.[10] AFM has presented an alternative way with which to study the interaction between a solid particle and a liquid droplet[11–13] and most recently between two emulsion droplets.[1,14–16] One of the advantages of the AFM technique is that the interaction between droplets of relatively small sizes (10–100 μm), characteristic of real emulsion systems, can be measured directly in static and dynamic force regimes. Recent advances in modeling the interaction between two droplets has allowed a quantitative interpretation of AFM force measurement data,[1,17–20] and previous studies have focused on the interactions between surfactant stabilized emulsion droplets at low electrolyte concentrations. In these cases, repulsive electric double layer (EDL) and hydrodynamic forces were dominant, whereas van der Waals interac-

* Corresponding authors. (F.G.) Tel.: +61-3-8344 6708; fax: +61-3-9347 5180; e-mail: franz@unimelb.edu.au. (R.R.D.) Tel.: +61-3-8344-4704; fax: +61-3-8344-4153; e-mail: rrd@unimelb.edu.au.
† School of Chemistry.
‡ Department of Chemical and Biomolecular Engineering.
§ Department of Mathematics and Statistics.

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tions were insignificant.[1,13] At elevated electrolyte concentrations, long-range EDL forces were screened, and according to the DLVO theory[21,22] of colloidal stability, two identical droplets should coalesce due to the action of the attractive van der Waals forces at small separations.

Our initial measurements of equilibrium interactions between two fluorocarbon droplets in the absence of surfactant additives showed that the interaction can be repulsive even at electrolyte concentrations as high as 0.1 M NaNO$_3$. Following these observations, we extended the measurements to include interactions between hydrocarbon oil droplets and between an oil droplet and a reference mica surface. Results presented here are interpreted within the framework of the DLVO theory and previously undertaken investigations that relate to the phenomenon associated with elevated electrolyte concentration, surfactant-free, emulsion film stability.

Experimental Procedures

The two types of nonpolar organic oils studied were C$_5$F$_{12}$ and C$_{14}$H$_{30}$. Purum grade C$_5$F$_{12}$ (3M product, commercial name Fluorinert Fluid PF-5050) and puriss grade C$_{14}$H$_{30}$ (99.5%+, olefine-free) were purchased from Fluka. The oils were further purified by passing them through a glass column filled with an activated magnesium silicate adsorbent (Florisil). This procedure was repeated several times. The final purity was evaluated by measuring the water−oil interfacial tension by means of the pendant drop method. Values for the interfacial tensions were obtained within 1 mN/m of literature values: 52 ± 1 mN/m for tetradecane−water and 56 ± 1 mN/m for perfluoropentane−water. Sodium nitrate (99+%, Aldrich) was baked at 250 °C for 5 h before being used to remove possible organic contaminations. All electrolyte solutions were made with Milli-Q water with an internal specific resistance no less than 18.2 MΩ/cm. The pH of the solution was adjusted by adding appropriate amounts of hydrochloric acid (HCl) or sodium hydroxide (NaOH) solutions.

A MFP-3D Asylum atomic force microscope (Asylum Research) and its attached fluid cell were used for all force measurements. Veeco tipless cantilevers (NP) were coated with Cr (1 to ~2 nm) and Au (10 to ~15 nm) and then immersed in 10 mM *n*-decanethiol (in ethanol) for at least 12 h to be hydrophobized.[23] The same procedure was used to hydrophobize the substrate (35 mm circular glass slides) used in the fluid cell. Oil drops were immobilized by spraying onto the hydrophobized substrate and were covered with the desired electrolyte (0.1 M NaNO$_3$) in the lower part of the fluid cell.[19] The cantilever was mounted on the upper fluid cell and then brought down toward the droplets on the substrate, at which point an appropriate droplet was chosen to be picked up by the cantilever tip.[15] This droplet was then aligned with another droplet from the substrate (or with the mica surface) with an optical microscope that captured the microscopic images of the droplets so the drop sizes could be estimated.

A schematic of the AFM two droplets force measurement experiment is shown in Figure 1. The droplets on the cantilever had diameters between 30−60 μm, whereas the droplets on the substrate had diameters between 50−200 μm. A Data Physics Tensiometer OCA 20 and its image analysis software SCA 20 were used to measure the contact angle of oil droplets immobilized on the previously mentioned substrate in 0.1 M NaNO$_3$ aqueous solutions. The contact angles were 41.30 ± 4 and 51.2 ± 4° for C$_{14}$H$_{30}$ and C$_5$F$_{12}$, respectively. In experiments that involved a mica surface, a piece of freshly cleaved muscovite mica was placed on the substrate after the droplets were formed on the original substrate to avoid contamination of the mica surface by the oil from dispersed oil drops. The fluid cell was then filled up with the remaining electrolyte,
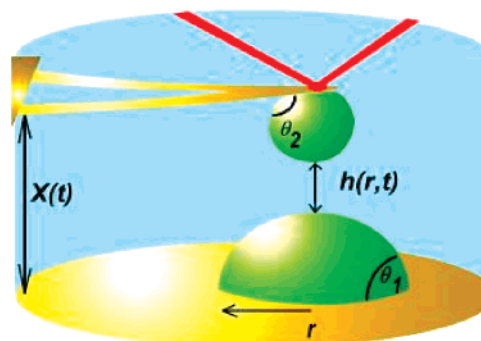

Figure 1. Schematic of the experiment between two oil droplets; one droplet is immobilized on the tipless cantilever, and the other one is immobilized on the substrate of an atomic force microscope.

and force measurements were made between the drop and the mica surface. Raw data were collected as a detector voltage output, which reflects the cantilever deflection versus relevant piezo motion. Conversion of the cantilever deflection voltage data (V) to force (nN) was performed using the standard procedure of multiplication by the AFM photodiode detector sensitivity (nm/V) and the measured cantilever spring constant (N/m). The nominal spring constant of the cantilevers used was 0.06 N/m, and using a thermal frequency method,[24] the exact values were found to be in the range of 0.06−0.07 N/m. The detector sensitivity was determined by pressing the bare cantilever against the substrate surface.

All parts of the Asylum fluid cell were rinsed with Milli-Q water, isopropyl alcohol, and ethanol and then dried with high purity nitrogen. All glassware used in the experiments was sonicated in 5% ABS laboratory detergent, rinsed with copious amounts of water, soaked in 10% nitric acid overnight, rinsed with Milli-Q water, and then dried in an oven. The fluid cell assembly process was carried out in a laminar flow cabinet to minimize contamination of the system.

Despite the rigorous precautions taken to purify the oils and the thorough cleaning of the fluid cell, experiments between oil phases without a stabilizing surfactant present and at elevated electrolyte concentrations are challenging. Even minimal contamination can alter the experimental outcome, which becomes even more an issue at increased electrolyte concentrations where the liquid films between interacting surfaces are very thin. To confirm the reproducibility of our data, each experimental condition (e.g., oil type, solution pH, and electrolyte concentration) was repeated several times and on each occasion with a different droplet. For the work reported, we limited our considerations to a maximum electrolyte concentration of 0.1 M.

The electrophoretic mobilities of C$_5$F$_{12}$ and C$_{14}$H$_{30}$ emulsion droplets were measured using a Brookhaven Electrokinetic Analyzer (Brookhaven Instruments Corp., PALS Zeta Potential Analyzer version 3.42). Emulsions were prepared in a Pyrex tube by vigorously shaking a mixture of the purified oil (about 0.1 wt % of the mixture content) and water phase followed by sonication in an ultrasonic cleaning bath for about 20 min. Before each measurement, the emulsion droplet concentration was adjusted to below 0.05 wt % by dilution with the water phase. The emulsion droplet size distributions were determined using a dynamic light scattering Malvern 4700 apparatus. The radii of the droplets ranged from 450 to 600 nm for the fluorocarbon emulsion at 0.1 M NaNO$_3$ and 500 to 900 nm for the C$_{14}$H$_{30}$ emulsion at the same ionic strength. The droplet radii were calculated assuming Stokes−Einstein diffusion for a droplet with internal flow.[25] The Brookhaven instrument measures the electrophoretic mobility of the emulsion droplet U_E. In most experiments, the ionic strength of the water phase was 0.1 M; therefore, the Debye screening length κ^{-1} was about 1 nm. For a rigid particle, the Smoluchowski formula[26] can be used to relate U_E

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to the ζ-potential since $\kappa a \gg 1$ (a is the droplet radius), but the conversion of electrophoretic mobility to the ζ-potential for bare oil droplets requires a different analysis than rigid particles.[27] The drop may have internal flow due to a nonzero tangential stress at the liquid−liquid interface. The internal flow reduces the viscous drag around the drop leading to a higher electrophoretic mobility than a rigid sphere for the same ζ-potential. The analysis methods developed by O'Brien and White[28] for a rigid particle and extended to liquid droplets by Ohsima et al.[27] were used to calculate the ζ-potential. These calculations were performed using a FORTRAN program called Mobility.[40]

As a consequence of the high electrolyte concentration, the emulsions were unstable over an extended period of time. Our general observation was that the instability was more pronounced for the $C_{14}H_{30}$ emulsions and increased as the pH decreased. Nevertheless, to obtain an adequate estimation for the ζ-potential of the droplets, the coagulation effects were minimized by working with highly diluted emulsions (0.01−0.03 wt %) and taking measurements in a short period following the sonication of the emulsion (10−15 min).

Results and Discussion

Droplet−Droplet Results. Initially, we investigated the interaction between C_5F_{12} (fluorocarbon) oil droplets in an aqueous electrolyte solution of 0.1 M NaNO$_3$ and for a range of pH values between 3.0 and 9.0. Typical results for the force, F, vs relevant piezo movement, ΔX, are given at pH 5.6 (Figure 2a) and pH 3.0 (Figure 2b) for both approach and retraction scans. The piezo drive velocity for the data presented was 100 nm/s. At this velocity, the absence of hysteresis between the approach and the retraction branches of the force curves indicates that hydrodynamic effects were negligible and that the force data can be considered to have been acquired under equilibrium conditions.[14] At pH 5.6, the interaction between the approaching droplets was entirely repulsive, and the force increased monotonically as ΔX decreased. The repulsive interaction between the drops suggests that they were always separated by a stable thin aqueous liquid film.[18] An almost exactly identical force curve to the one shown in Figure 2a for pH 5.6 was observed for the solution at pH 9.0.

A different outcome was observed when the measurements were performed at low pH (3.0). As the droplets were brought together, a small repulsive force developed before the two droplets coalesced as indicated by the cantilever jump-in position terminating the approaching force curve in Figure 2b. The same type of pH dependence represented in Figure 2, namely, repulsion between the droplets at pH 5.6−9.0 and a small initial repulsion followed by droplet coalescence at pH 3.0, was observed in several different experiments and using a range of droplets sizes of about 30−60 μm for the cantilever droplet diameter and 50−200 μm for the substrate droplet diameter. A few experiments were also conducted for solutions at lower electrolyte concentrations, of 10^{-2} NaNO$_3$ and pH 5.6, and the interactions between the droplets was found to be entirely repulsive as well.

The same type of measurements as described previously were repeated for two hydrocarbon ($C_{14}H_{30}$) oil droplets in an aqueous electrolyte solution of 0.1 M NaNO$_3$. As in the case of the fluorocarbon droplets, interaction at high pH (9.0) was found to be purely repulsive (Figure 3a).

However, unlike the fluorocarbon system, the hydrocarbon droplets jumped into contact immediately at close approach at
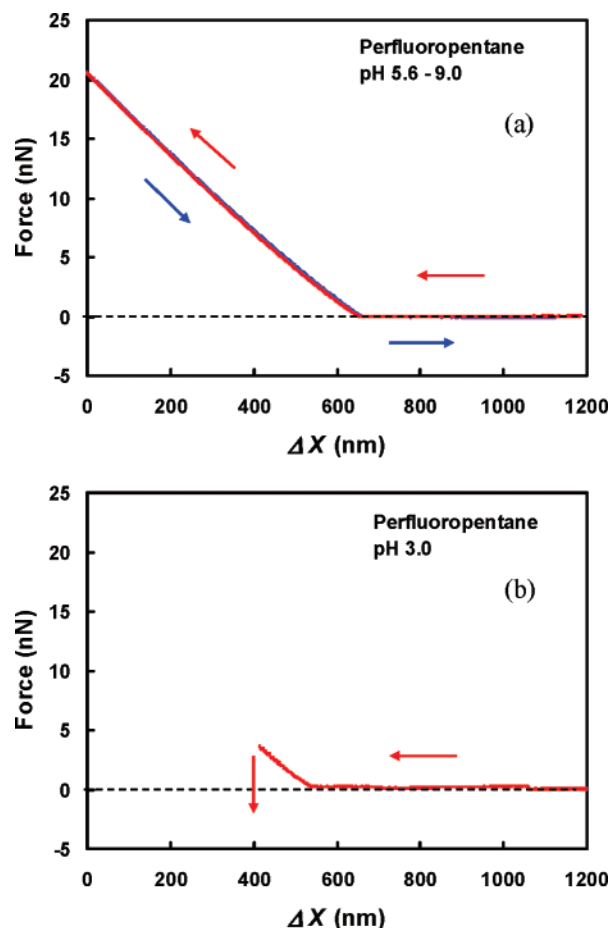
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Figure 2. Typical interaction force, F, vs relevant piezo motion, ΔX, measured between two C_5F_{12} droplets in 0.1 M NaNO$_3$ aqueous solution: (a) at pH 5.6−9.0 and (b) at pH 3.0. The arrows indicate the droplet approach (red) and retraction (blue). Droplet diameters were about 30 μm for the cantilever and 60 μm for the substrate.

pH 3.0−5.6 (Figure 3b) without exhibiting signs of any initial weak repulsion. Some experiments were then carried out for 10^{-2} M NaNO$_3$ pH 5.6, and the interaction was found to be entirely repulsive.

A common result for both oil systems was that, depending on the solution pH, the interaction between the approaching droplets could be entirely repulsive. For interactions between oil droplets at lower electrolyte concentrations, such behavior is not unexpected as previous ζ-potential measurements have shown that the oil−water interface can be significantly charged even in the absence of additives.[2−4] Provided certain pre-conditioning procedures are applied, related to degassing the water phase, this charge has been used to account for the stability of surfactant-free emulsions.[29,30] However, the formation of stable emulsion surfactant-free systems at ionic strengths as high as 0.1 M is unexpected. At that ionic strength, the stabilizing EDL force is extremely short-ranged, with a Debye length of only 0.96 nm. It can be expected that the magnitude of EDL interactions would not be sufficiently large to prevent the droplet surfaces from approaching to within the range of the attractive van der Waals force. To facilitate a quantitative comparison between the observed force behavior and the predictions of the DLVO theory, it was necessary to measure the electrophoretic mobility and hence determine the ζ-potential of the fluorocarbon and hydrocarbon emulsion droplets at the same solution conditions

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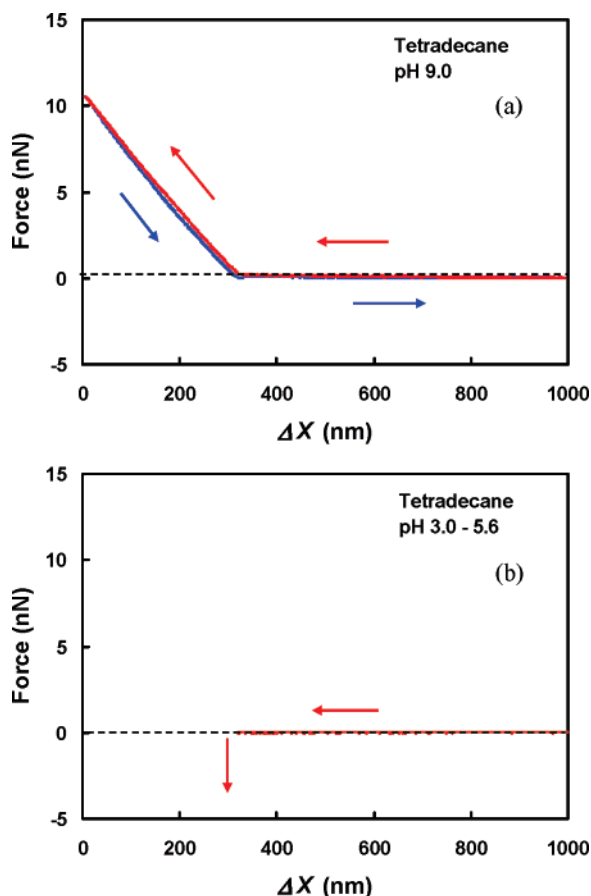Figure 3. Typical interaction force, F, vs relevant piezo motion, ΔX, measured between two $C_{14}H_{30}$ droplets in the presence of 0.1 M NaNO₃: (a) at pH 9.0 and (b) at pH 3.0−5.6. Droplet diameters were about 40 μm for the cantilever and 50 μm for the substrate.

Table 1. Measured ζ-Potentials (mV) of Droplets of Oils Studied in 0.1 M NaNO₃ and Different pH Values[a]

pH	C_5F_{12}	$C_{14}H_{30}$
9.0	$-19 \pm 4 \, (-1.98)$	$-26 \pm 4 \, (-2.11)$
5.6	$-12 \pm 3 \, (-1.31)$	$-17 \pm 3 \, (-1.35)$
3.0	(low)	(low)

[a] In parentheses is given the corresponding average electrophoretic mobility $\times 10^8$ (m² V⁻¹ s⁻¹).

as in our force experiments. The results, summarized in Table 1, show that both types of oils have a similar charge, which can be as high as about -30 mV at pH 9.0. The range of ζ-potential values and the dependence on the pH are in reasonable agreement with literature values.[2−4] The possible origin of the surface charge on oil droplets has been previously, carefully, investigated, and it was concluded that it was due to the spontaneous adsorption of hydroxyl ions at the water−oil interface,[2] although the physical reasons for that adsorption remain elusive.[4,31]

The measured values of the maximum ζ-potentials allow us to estimate if the observed force behavior could be explained in the framework of the DLVO theory. A detailed analysis of the AFM equilibrium force measurements, involving deformable surfaces interacting with DLVO forces, is provided elsewhere for both particle−droplet interactions[12,17,18] and droplet−droplet interactions,[16] but a simplified result is used. For the case where repulsive forces are observed in the AFM measurements, the inter-droplet separation approaches a limiting value in the higher
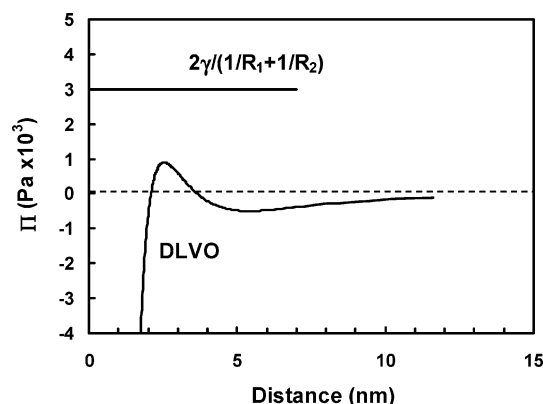
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Figure 4. DLVO disjoining pressure between flat interfaces constructed from the sum of the van der Waals interaction calculated for the hydrocarbon−water system and EDL force from a numerical solution to the Poisson−Boltzmann equation with a constant surface charge boundary condition at an electrolyte strength of 0.1 M ($\psi_0 = -30$ mV and $A = 0.33 \times 10^{-20}$ J). The horizontal solid line is the estimation of the minimal Laplace pressure in the system ($R_1 = 50$ μm, $R_2 = 100$ μm, and $\gamma = 51$ mN/m).

force range. This is because the interfaces begin to flatten as the disjoining pressure between the interfaces becomes comparable to the Laplace pressure difference in the droplets, according to

$$\Pi(D_L) = 2\gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \quad (1)$$

where R_1 and R_2 are the radius of curvature of the droplets, γ is the oil−water interfacial tension, and $\Pi(D_L)$ the disjoining pressure between the two flat oil−water interfaces at a limiting separation D_L. The DLVO disjoining pressure between two flat interfaces was constructed as the sum of the attractive van der Waals force and the repulsive EDL force. To obtain an estimate for the upper limit case in the repulsive barrier maximum, the EDL force was calculated for constant charge boundary conditions, and taking the highest ζ-potential value for the surface potential, $\psi_0 = -30$ mV. Calculations were performed by numerically solving the Poisson−Boltzmann equation, using the algorithm of Chan et al.[32] The van der Waals interaction was estimated using a non-retarded Hamaker constant of $A = 0.33 \times 10^{-20}$ J, calculated from the optical properties (dielectric constant and refractive index)[33] of $C_{14}H_{30}$ and water. Approximately the same value was obtained for the C_5F_{12} and water system. The resulting upper limit DLVO disjoining pressure profile is given in Figure 4. A characteristic lower limit value for the Laplace pressure in the system was estimated based on the typical radius of curvature of the largest droplets used in our measurements: $R_1 = 50$ μm for the cantilever drops, $R_2 = 100$ μm for substrate droplets (estimated from the droplet size and contact angle), and interfacial surface tension value $\gamma = 51$ mN/m for tetradecane−water ($\gamma = 56$ mN/m for perfluoropentane−water). The estimated value of the lower Laplace pressure is shown as the horizontal solid line in Figure 4. The comparison indicates that even for the upper limit case of the EDL force, the DLVO disjoining pressure maximum is significantly lower than the lower limit Laplace pressure. Indeed, these differences are even more strongly pronounced for the case of the fluorocarbon at normal pH, constant potential boundary conditions, smaller R droplets, etc. Therefore, DLVO forces alone cannot explain the repulsive force behavior observed between these oil droplets.

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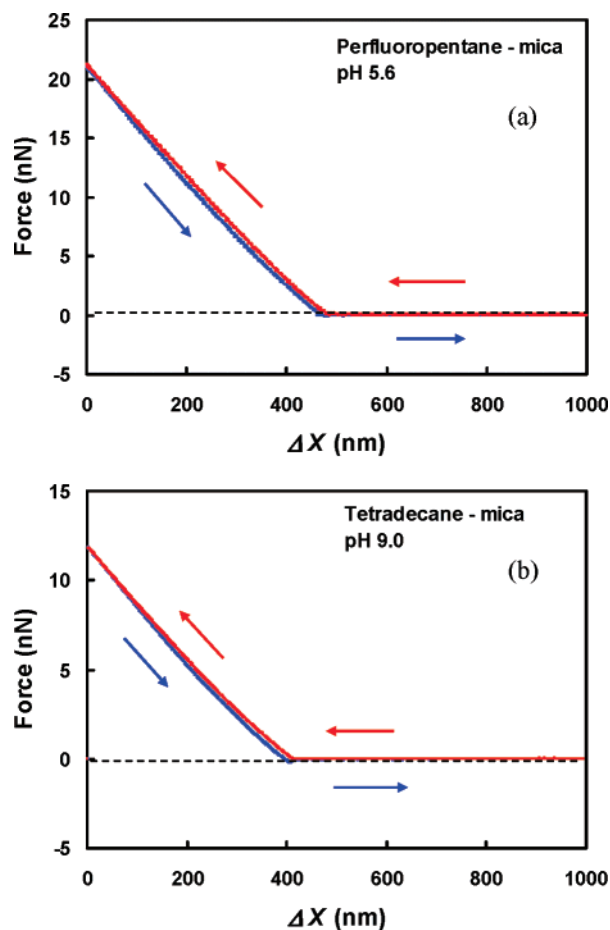
Figure 5. Measured interaction force, F, vs relevant piezo motion, ΔX, between a mica surface and (a) a C_5F_{12} oil droplet at pH 5.6 and (b) a $C_{14}H_{30}$ oil droplet at pH 9.0 in 0.1 M NaNO$_3$ aqueous solution. Droplet diameters were about 25 μm (a) and 35 μm (b).

Figure 6. Measured interaction force, F, vs relevant piezo motion, ΔX, between a mica surface and (a) a C_5F_{12} oil droplet and (b) a $C_{14}H_{30}$ oil droplet at pH 3.0 in 0.1 M NaNO$_3$ aqueous solution. Droplet diameters were about 40 μm (a) and 25 μm (b).

The extra repulsive force revealed by our experiments resembles the hydration repulsive force characteristic for the interaction between charged hydrophilic surfaces in aqueous electrolyte solutions.[34] Surface force apparatus (SFA) measurements of the interaction between mica surfaces in monovalent electrolyte solutions have shown the existence of a short-range repulsive force that can prevent the adhesive contact of surfaces.[35] That short-range interaction was primarily attributed to the excess energy necessary to dehydrate the cations adsorbed on the mica surfaces at higher electrolyte concentrations.[33−35] Other corrections related to the charges present on the oil surfaces that could affect the interaction could be the excluded volume of the hydrated electrolyte ions[36] and induced polarization.[37] The surfactant-free nonpolar oils we investigated, as already indicated, do not have their own charge and are generally regarded as strongly hydrophobic. However, as mentioned earlier, the surfaces become charged due to the spontaneous adsorption of hydroxyl ions, and it is possible that the extra repulsive force observed could be related to some type of hydration force phenomenon associated with these charges. At high electrolyte concentrations, the hydroxyl groups may be able to attract hydrated cations or could themselves induce water bound structures. To probe how the extra repulsive force could relate to the repulsive hydration force found at solid surfaces, we performed a series of measurements between an oil droplet and a mica substrate. An additional
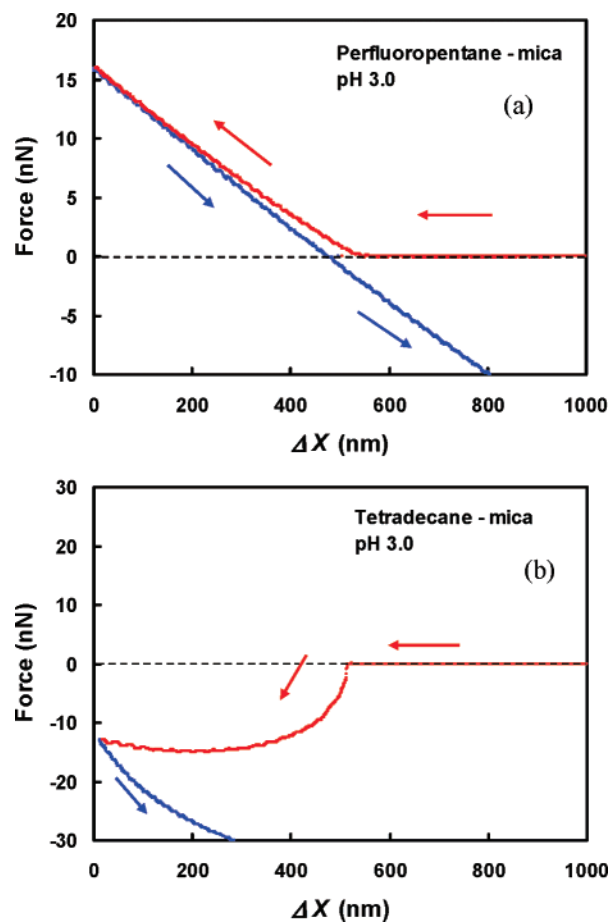
motivation for these experiments was the expectation that for the fluorocarbon−water−mica system, the usually attractive van der Waals interaction should be repulsive.

Droplet−Mica Results. Results for the interaction of an oil droplet and a mica surface in a 0.1 M NaNO$_3$ aqueous solution are summarized in Figures 5 and 6. Similar interaction pH dependences were found as in the case of droplet−droplet interactions. For the fluorocarbon oil and mica system, an entirely repulsive force was measured at pH 5.6 (Figure 5a), and the same was observed at a higher pH (9.0). For the hydrocarbon droplet, the force was still repulsive at high pH (9.0) (Figure 5b), but the droplet jumped into contact with the mica surface at pH 5.6. As we have already noted, behind the short-range non-DLVO repulsive forces, for the case of the mica−fluorocarbon interaction, the van der Waals interaction could be an additional stabilizing factor. On the basis of the optical properties of the mica−water−perfluoropentane system, a Hamaker constant of $A = -0.9 \times 10^{-20}$ J was estimated, corresponding to a repulsive van der Waals force and for the case of the tetradecane−water−mica system, the value was $A = 1.2 \times 10^{-20}$ J.[33] If one considers the experimental results of the fluorocarbon−mica alone, it might appear that they indicate the existence of a repulsive van der Waals force stabilization. However, bearing in mind the results from the fluorocarbon−fluorocarbon droplet interaction and the tetradecane−mica system at high pH, it is difficult to disentangle the van der Waals contribution from that of the extra repulsive non-DLVO force. In that respect, the experiments carried out at low pH (3.0) were intriguing as the droplet−droplet interactions were attractive. During the approach of the droplets to the mica

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Table 2. Summarized Results for AFM Force Measurement between Fluorocarbon and Hydrocarbon Droplets and Droplet and Mica Surface in 0.1 M NaNO₃ Aqueous Solution

system	pH 3.0	pH 5.6	pH 9.0
hydrocarbon to hydrocarbon	No repulsion, just coalescence	no repulsion, just coalescence	all repulsive, no hysteresis
hydrocarbon to mica	No repulsion, just coalescence	no repulsion, just coalescence	all repulsive, no hysteresis
fluorocarbon to fluorocarbon	small repulsion, then coalescence	all repulsive, no hysteresis	all repulsive, no hysteresis
fluorocarbon to mica	repulsive on approach, attractive on retraction	all repulsive, no hysteresis	all repulsive, no hysteresis

surface, there was a noticeable difference in the force profile between the fluorocarbon and hydrocarbon oil cases, given in Figure 6a,b, respectively. As expected, the $C_{14}H_{30}$ drop collapsed over the mica surface immediately after contact, pulling the cantilever down, which can be interpreted as spreading the drop over the surface. On the other hand, in the case of the fluorocarbon oil, during the approach movement, the interaction appeared entirely repulsive; however, during the retraction, a hysteresis appeared followed by an adhesive pull, indicating that the drop had come in direct contact with the surface. It would appear that for the fluorocarbon−mica system, the van der Waals interaction alone cannot provide film stability. A possible reason for this could be that at low pH, the surface charges are significantly removed and the fluorocarbon surface behaves like a hydrophobic surface, inhibiting the destabilization of the water thin liquid film in its vicinity.[33] A previous attempt to measure repulsive van der Waals interactions across an aqueous film between a gold and a solid fluorocarbon (Teflon) surface showed an attractive interaction, but the purity of the experimental conditions was queried.[38]

Results from our AFM force measurement experiments are listed in Table 2. The mica−oil droplet experiments support the implications of the droplet−droplet experiments in that a non-DLVO repulsive force of the same type as the hydration force between hydrophilic surfaces was present on the charged nonpolar oil surfaces. The strong dependence of that force on the solution pH suggests that it is associated with the surfaces being charged by hydroxyl ions and hydrated cations. The extra force was strongly pronounced for the case of fluorocarbon oils, although the physical reason for that is unclear at present. An interesting similarity might exist between surfactant-free nonpolar oil droplets and air bubbles, which are believed to have a similar mechanism

of surface charging in the absence of charged surfactant additives. It was previously found that the presence of an electrolyte (typical at concentrations above 0.1 M) can significantly inhibit the bubble coalescence rate depending on the type of the electrolyte.[39] To investigate this possibility in the future, it will be necessary to examine a wider number of nonpolar surfactant-free oil interactions, including different types of electrolytes and over an extended concentration range. As compared to bubbles, the case of oil droplets could be more complicated as the water phase contains dissolved gases that could strongly affect the interaction and consequently the emulsion stability.[29]

Conclusion

The force of interaction between two identical fluorocarbon or hydrocarbon droplets in a water electrolyte solution of 0.1 M NaNO₃ and in the absence of surfactant has been measured. It was found that the interaction between two fluorocarbon droplets was repulsive at normal to high pH values (5.6−9.0) and attractive at low pH (3.0). For the hydrocarbon droplets, the interaction was repulsive at high pH (9.0) but attractive at low to medium pH (3.0−5.6). This pH dependence follows a similar trend as did the droplet ζ-potentials. Comparison with the predicted force profile as a DLVO interaction could not explain the observed film stability. Experiments between droplets and a mica surface further confirmed the operation of a non-DLVO repulsive force and to a certain extent were correlated with the van der Waals forces in these systems. We suggest that the observed extra repulsive force observed was related to the charging of the oil surface by adsorbed hydroxyl ions and possibly hydrated cations.

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